Inductive Effect of Adjacent Groups on the Symmetrical Deformation and the Rocking Frequencies of Methyl Groups

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Inductive Effect of Adjacent Groups on the Symmetrical Deformation and the Rocking Frequencies of Methyl Groups*

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The symmetrical deformation and the rocking frequencies of the CH_3 group, δ_{CH_3} and γ_{CH_3}, in $(CH_3)_nXH_{m-n}$ molecules and those of the CD_3 group, δ_{CD_3} and γ_{CD_3}, in the deuterium derivatives are studied in relation to the type of X atom in the groups IV—VII of the periodic table, where m is the valence of X atom and n an integer from 1 to m. The frequency shifts of these vibrations are ascribed to the change in the force constant for the deformation of the HCX angle, and are expressed as

$$\delta_{CH_3} = 375 \log (x_X/r^2_{CX}) + 1366 \quad \text{(a)}$$

$$\gamma_{CH_3} = 582 \log (x_X/r^2_{CX}) + 1045 \quad \text{(b)}$$

$$\delta_{CD_3} = 338 \log (x_X/r^2_{CX}) + 1049 \quad \text{(c)}$$

$$\gamma_{CD_3} = 416 \log (x_X/r^2_{CX}) + 778 \quad \text{(d)}$$

for all deuterated and undeuterated molecules examined except for some cases where considerable coupling seems to exist between these and other modes of vibrations. Here x_X represents the electronegativity of the X atom and r_{CX} the C—X bond length. The correlation between the formulas (a) and (c), and that between (b) and (d) can be theoretically interpreted by taking into consideration the change of the kinetic energy matrix on deuteration of the methyl group.

If these formulas are assumed to hold for the molecules such as CH_3NO_2 and CH_3CCl_3, the group electronegativity of the radical directly attached to the methyl group is derived from the symmetrical deformation and the rocking frequencies observed for the molecule. The results are compared with other sets of group electronegativities obtained empirically from various spectorscopic relations.

1. INTRODUCTION

Vibrational spectra of the methyl compounds have been the subject of many investigations and a considerable amount of experimental data has been accumulated concerning the deformation frequencies of the methyl group. From these data it is coucluded that the symmetrical deformation and the rocking frequencies of the methyl groups are very sensitive to the type of the adjacent atom whereas the degenerate deformation frequency is insensitive.

Nakagawa and Mizushima[1] calculated the hydrogen deformation frequencies of various organic compounds and pointed out that the frequency shifts of both

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the symmetrical deformation and the rocking vibrations of the CH_3X group were ascribed to the change in the deformation force constant F_{HCX} of the HCX angle. Accordingly two deformation frequencies may be expected to depend upon some structural parameters of the C–X bond in a nearly analogous fashion.

Some attempts were made on this subject. Bellamy and Williams[2] studied the correlation between six fundamental frequencies of the methyl halides, and suggested that there was an intimate relation between the symmetrical deformation and the rocking frequencies. Wilmshurst[3] showed that, when the respective squares of two frequencies of the methyl halides were plotted against the electronegativity of the halide atom, nearly parallel straight lines were obtained. Sheppard[4] also found that plots of the symmetrical deformation frequency of the CH_3X group against the electronegativity of X atom gave a set of approximately parallel straight lines with elements from the same row in the periodic table falling on the same line. Recently, King and Crawford[5] pointed out that the CH_3 and CD_3 symmetrical deformation frequencies of the CH_3X and CD_3X group were roughly proportional to the parameter $(x_X/r_{CX}^2)^{3/8}$, where x_X is the electronegativity of the X atom and r_{CX} the C–X bond length.

In the present report, the symmetrical deformation and the rocking frequencies of the $(CH_3)_nXH_{m-n}$ molecules and its deuterium derivatives are studied in relation to the type of the X atom in the groups IV–VII of the periodic table, and the linear dependence of these frequencies upon the parameter $\log(x_X/r_{CX}^2)$ is found. Here m is the valence of the X atom and n an integer from 1 to m. A comparison between the relation of the present authors and that of King and Crawford[5] shows that the former surpasses the latter in linearity as is seen later. Furthermore, on the assumption that the linear relations obtained for the $(CH_3)_nXH_{m-n}$ molecules can be extended to other methyl compounds, the group electronegativity of the radical directly attached to the methyl group in the molecules such as CH_3NO_2 and CH_3CCl_3 is derived. The results are compared with other sets of group electronegativities obtained from various relations.

2. THE SYMMETRICAL DEFORMATION AND THE ROCKING FREQUENCIES AND SOME PARAMETERS OF LINKAGE

2.1 The Symmetrical Deformation and the Rocking Frequencies of Methyl Groups

From normal coordinate calculations for a number of molecules with the CH_3X group, Siebert[6] noticed that the deformation force constant F_{HCX} was roughly proportional to the C–X stretching force constant K_{CX}. Accordingly, when it is remembered that the symmetrical deformation and the rocking frequencies of the CH_3X groups vary with F_{HCX}, these frequencies may be expected to be related to K_{CX}. In fact, for the methyl halides, the simple (non-linear) dependence of these frequencies upon the square root of K_{CX} is suggested in the report of Bellamy and Williams[2] though they did not point out explicitly. On

the other hand, according to Gordy[7], K_{CX} of the simple molecules with the CH_3X group is shown by an empirical formula of the form

$$K_{CX} = aN(x_C x_X / r_{CX}^2)^{3/4} + b\,, \qquad (1)$$

where x_C and x_X are the electronegativities of C and X atoms forming the bond, N and r_{CX} are the bond order and the bond length, and a and b are constants for certain broad classes of molecules. Then the symmetrical deformation and the rocking frequencies of the methyl compounds may be expressed as some function of x_X/r_{CX}^2, a factor concerning X in the right-hand side of Eq. (1).

In order to test this argument, two frequencies of the $(CH_3)_nXH_{m-n}$ and $(CH_3)_nXD_{m-n}$ molecules are collected for the X atom in groups IV–VII of the periodic table as many as possible and summarized in Table 2. These frequencies have now been reliably identified in the infrared and Raman spectra of many molecules. Almost all data in Table 2 were obtained in the gaseous state except for some Raman data, which were measured in the liquid state.

In general, when a molecule contains n methyl groups, n symmetrical deformation vibrations and $2n$ rocking vibrations are expected for the molecule. These vibrations divide into respective symmetry species, according to the symmetry of the molecule. In Table 1, the symmetry species of the symmetrical deformation and the rocking vibrations of various $(CH_3)_nXH_{m-n}$ molecules are shown together with their activities in infrared and Raman spectra. In the fifth and ninth columns of Table 2, the separate frequencies and their symmetry species as assigned in the literature are listed for the symmetrical deformation and the rocking vibrations. Next respective columns are the average values, δ_{CH_3} and γ_{CH_3}, of the symmetrical deformation and the rocking frequencies. In calculating the averages, the degeneracies are taken into account.

To obtain the value of x_X/r_{CX}^2, Gordy's electronegativity[8] defined as the electric potential at the covalent boundary of an atom, and the bond length[9] obtained by means of the microwave spectrum and the electron diffraction experiment of the gaseous substance are used (third and fourth columns of Table 2).

Table 1. Symmetry of $(CH_3)_nXH_{m-n}$ molecules and symmetry species of the symmetrical deformation and the rocking vibrations of methyl groups.

Number of methyl groups in a molecule	Symmetry of molecule (Example)	Symmetry species (Activity)[a]	
		Sym. deformation vibration	Rocking vibration
1	$C_{3v}(CH_3F)$	A_1(I, R)	E(I, R)
	$C_s(CH_3OH,\ CH_3NH_2)$	A'(I, R)	A'(I, R)+A''(I, R)
2	$C_{2v}((CH_3)_2O,\ (CH_3)_2CH_2)$	A_1(I, R)+B_1(I, R)	A_1(I, R)+A_2(R)+B_1(I, R)+B_2(I, R)
	$C_s((CH_3)_2PH)$	A'(I, R)+A''(I, R)	2A'(I, R)+2A''(I, R)
	$D_{3d}(CH_3CH_3)$	A_{1g}(R)+A_{2u}(I)	E_g(R)+E_u(I)
3	$C_{3v}((CH_3)_3N,\ (CH_3)_3CH)$	A_1(I, R)+E(I, R)	A_1(I, R)+A_2+2E(I, R)
4	$T_d((CH_3)_4C)$	A_1(R)+F_2(I, R)	E(R)+F_1+F_2(I, R)

Note: a) I and R mean infrared active and Raman active respectively.

The bond length of $(CH_3)_nXD_{m-n}$ molecule is assumed to be the same as that of the corresponding $(CH_3)_nXH_{m-n}$ molecule.

In Fig. 1 are given the plots of δ_{CH_3} and γ_{CH_3} against the parameter $\log(x_X/r_{CX}^2)$ where all points fall closely along respective straight lines given by

$$\delta_{CH_3} = 375 \log(x_X/r_{CX}^2) + 1366 \qquad (2)$$

and

$$\gamma_{CH_3} = 582 \log(x_X/r_{CX}^2) + 1045 . \qquad (3)$$

In order to compare these relations with that of King and Crawford[5], δ_{CH_3} and γ_{CH_3} are plotted against their parameter $(x_X/r_{CX}^2)^{3/8}$ using the data of Table 2, and the slightly curved lines are obtained as is seen in Fig. 2.

The values calculated from Eqs. (2) and (3), which are listed in seventh and eleventh columns of Table 2, are compared with the corresponding observed average frequencies. From the percent deviations (eighth and last columns) of all molecules examined, the mean square deviation* 0.9% for the symmetrical deformation frequency and 1.9% for the rocking frequency are obtained, showing nearly good agreement between the observed average and calculated values. The fact that the latter is larger than the former may be due to the greater coupling of the rocking vibration than of the symmetrical deformation vibration.

For CH_3NH_2 (point group C_s) which shows a relatively large deviation of the rocking frequency, it was reported by Yamaguchi[10] that there are considerable couplings among the A' CH_3 rocking, the A' CH_3 degenerate deformation and NH_2 wagging vibrations, and between the A'' CH_3 rocking and the A'' CH_3 degenerate deformation vibrations. For CH_3ND_2 (point group C_s), Gray and Lord[11] tentatively assigned the A'' CH_3 rocking vibration to a broad band observed at 1187 cm^{-1}, but Yamaguchi[10] identified this vibration with a band at 1140 cm^{-1} according to the results of the potential energy distribution in the molecule. The average frequency obtained by using the latter as the A'' rocking frequency is in very good agreement with the value calculated from Eq. (3) (Table 2).

The observed average rocking frequency of CH_3CH_3 also shows a large deviation from the calculated value. Since, from the normal coordinate calculation for CH_3CH_3 and CD_3CD_3 Nakagawa[12] pointed out that all of the fundamentals of above two molecules were nearly pure, the deviation of the observed rocking frequency in CH_3CH_3 cannot be explained on a basis of the coupling. Thus further investigations are required to clear up this point.

Since δ_{CH_3} and γ_{CH_3} are related linearly to $\log(x_X/r_{CX}^2)$, the plot of δ_{CH_3} against γ_{CH_3} should yield a straight line. This is justified in Fig. 3.

The fact that both δ_{CH_3} and γ_{CH_3} are linear functions of $\log(x_X/r_{CX}^2)$ may be interpreted by considering that δ_{CH_3} and γ_{CH_3} depend upon the deformation force constants, F_{HCX} and F_{HCH}, of the valence angle HCX and HCH in the forms[1]

* $\left\{\overline{(\text{percent deviation})^2}\right\}^{1/2}$

Table 2. Observed and calculated frequencies of the symmetrical deformation and

(1) No.	(2) Molecule	(3) Electro-negativity[a] x_X	(4) Bond length[b] r_{CX} (Å)	Sym. CH_3 deformation frequency (cm^{-1})		
				(5) Observed (Species)	(6) Average	(7) Calculated
1	CH_3F	3.94	1.39	1468 (A_1)[d]	1468	1482
2	CH_3OH	3.47	1.43	1455 (A')[e]	1455	1452
3	CH_3OD	3.47	1.43	1458 (A')[e]	1458	1452
4	$(CH_3)_2O$	3.47	1.43	1450 (A_1, B_1)[f]	1450	1452
5	CH_3NH_2	3.01	1.47	1430 (A')[g]	1430	1420
6	CH_3ND_2	3.01	1.47	1430 (A')[g]	1430	1420
7	$(CH_3)_3N$	3.01	1.47	1404 (A_1, E)[h]	1404	1420
8	CH_3CH_3	2.52	1.54	1400 (A_{1g}) 1379 (A_{2u})[i]	1390	1376
9	$(CH_3)_2CH_2$	2.52	1.54	1370 (A_1) 1375 (B_1)[j]	1373	1376
10	$(CH_3)_2CD_2$	2.52	1.54	1380 (A_1, B_1)[k]	1380	1376
11	$(CH_3)_3CH$	2.52	1.54	1394 (A_1) 1370 (E)[l]	1378	1376
12	$(CH_3)_3CD$	2.52	1.54	1394 (A_1) 1370 (E)[l]	1378	1376
13	$(CH_3)_4C$	2.52	1.54	1370 (A_1, F_2)[m]	1370	1376
14	CH_3Cl	3.00	1.78	1355 (A_1)[d]	1355	1357
15	CH_3SH	2.58	1.82	1335 (A')[n]	1335	1326
16	$(CH_3)_2S$	2.58	1.82	1324 (A_1, B_1)[f]	1324	1326
17	$(CH_3)_2PH$	2.19	1.87[c]	1297 (A') 1281 (A'')[o]	1289	1290
18	$(CH_3)_3P$	2.19	1.87	1312 (A_1) 1293 (E)[h]	1299	1290
19	$(CH_3)_4Si$	1.82	1.89	1254 (A_1, F_2)[m]	1254	1256
20	CH_3Br	2.68	1.94	1305 (A_1)[d]	1305	1311
21	$(CH_3)_2Se$	2.35	1.98	1282 (A_1, B_1)[f]	1282	1283
22	$(CH_3)_3As$	2.04	1.98	1263 (A_1) 1242 (E)[h]	1249	1260
23	$(CH_3)_4Ge$	1.77	1.98	1247 (A_1) 1234 (F_2)[p]	1237	1237
24	CH_3I	2.36	2.14	1252 (A_1)[d]	1252	1258
25	$(CH_3)_3Sb$	1.82	2.18[c]	1213 (A_1) 1194 (E)[h]	1200	1210
26	$(CH_3)_4Sn$	1.61	2.18	1205 (A_1) 1194 (F_2)[p]	1197	1190
27	$(CH_3)_3Bi$	1.83	2.29[c]	1165 (A_1) 1147 (E)[h]	1153	1195
28	$(CH_3)_4Pb$	1.56	2.29	1170 (A_1) 1154 (F_2)[p]	1158	1169

Note: a) Reference 8).
b) Reference 9).
c) Since no data is found in reference 9), the sum of Pauling's covalent radii is used. [L. Pauling, "The Nature of the Chemical Bond" chap. 7, Cornell Univ. Press, Ithaca, New York (1960)].
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e) Reference 13).
f) H. Siebert, *Z. anorg. u. allgem. Chem.*, **271**, 65 (1952).
g) Reference 11).
h) H. Siebert, *Z. anorg. u. allgem. Chem.*, **273**, 161 (1953).
i) G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952).

the rocking vibrations of CH_3 groups in $(CH_3)_nXH_{m-n}$ and $(CH_3)_nXD_{m-n}$ molecules.

(8) Deviation 100{(6)−(7)}/(6) (%)	CH_3 rocking frequency (cm^{-1})			(12) Deviation 100{(10)−(11)}/(10) (%)
	(9) Observed (Species)	(10) Average	(11) Calculated	
−0.9	1200 (E)[d]	1200	1225	−2.1
+0.2	1116 (A') 1233 (A'')[e]	1175	1178	−0.3
+0.4	1160 (A') 1228 (A'')[e]	1194	1178	+1.3
−0.1	1239 (A_1) 1112 (A_2) 1194 (B_1) 1160 (B_2)[f]	1176	1178	−0.2
+0.7	1130 (A') 1195 (A'')[g]	1163	1129	+2.9
+0.7	1117 (A') 1140[q] (A'')[g]	1129	1129	0
−1.1	1184 (A_1) 1104 (E)[h]	1131	1129	+0.2
+1.0	1190 (E_g) 822 (E_u)[i]	1006	1060	−5.4
−0.2	1152 (A_1) 1278 (A_2) 1053 (B_1) 748 (B_2)[j]	1058	1060	−0.2
+0.3	——	—	1060	—
+0.1	——	—	1060	—
+0.1	——	—	1060	—
−0.4	925 (E, F_1) 1280 (F_2)[m]	1058	1060	−0.2
−0.1	1015 (E)[d]	1015	1031	−1.6
+0.7	957, 1060 (A', A'')[n]	1008	982	+2.6
−0.1	1042 (A_1) 1014 (A_2) 1015 (B_1) 1030 (B_2)[f]	1025	982	+4.2
−0.1	948, 922 (A') 964, 857 (A'')[o]	898	927	−3.2
+0.7	973 (A_1) 948 (E)[h]	956	927	+3.0
−0.1	869 (E, F_1, F_2)[m]	869	875	−0.7
−0.5	954 (E)[d]	954	959	−0.5
−0.1	921 (A_1) 911 (A_2) 914 (B_1) 916 (B_2)[f]	916	916	0
−0.9	884 (A_1, E)[h]	884	881	+0.3
0	825 (E, F_1, F_2)[p]	825	844	−2.3
−0.5	880 (E)[d]	880	877	+0.3
−0.8	813 (A_1, E)[h]	813	803	+1.2
+0.6	772 (E_1, F_1, F_2)[p]	772	772	0
−3.6	784 (A_1, E)[h]	784	779	+0.6
−0.9	700 (E) 765 (F_1) 767 (F_2)[p]	750	740	+1.3

j) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York (1949).
k) H. L. McMurry and V. Thornton, *J. Chem. Phys.*, **19**, 1014 (1951).
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m) C. W. Young, J. S. Koehler and D. S. McKinney, *J. Am. Chem. Soc.*, **69**, 1410 (1947).
n) H. W. Thompson and N. P. Skerrett, *Trans. Faraday Soc.*, **36**, 812 (1940).
o) H. C. Beachell and B. Katlafsky, *J. Chem. Phys.*, **27**, 182 (1957).
p) E. R. Lippincott and M. C. Tobine, *J. Am. Chem. Soc.*, **75**, 4141 (1953).

q) The value (1187 cm^{-1}) of reference 11) is replaced by this value, according to the result[10] of the potential energy distribution in this molecule (see text).

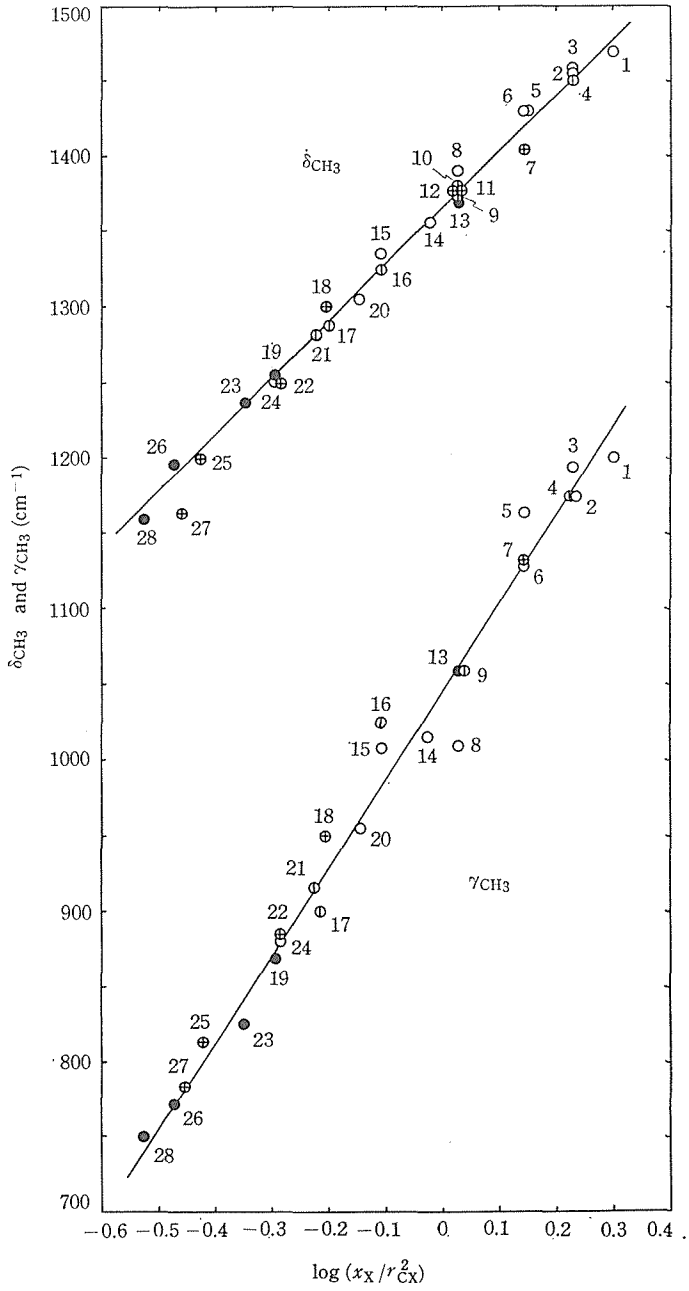

Fig. 1. Plot of δ_{CH_3} and γ_{CH_3} against log (x_X/r^2_{CX}) for $(CH_3)_nXH_{m-n}$ and $(CH_3)_nXD_{m-n}$ molecules.

Numbers beside plots are those of molecules in Table 2.
○ : n=1, ◑ : n=2, : ⊕ n=3, ● : n=4.

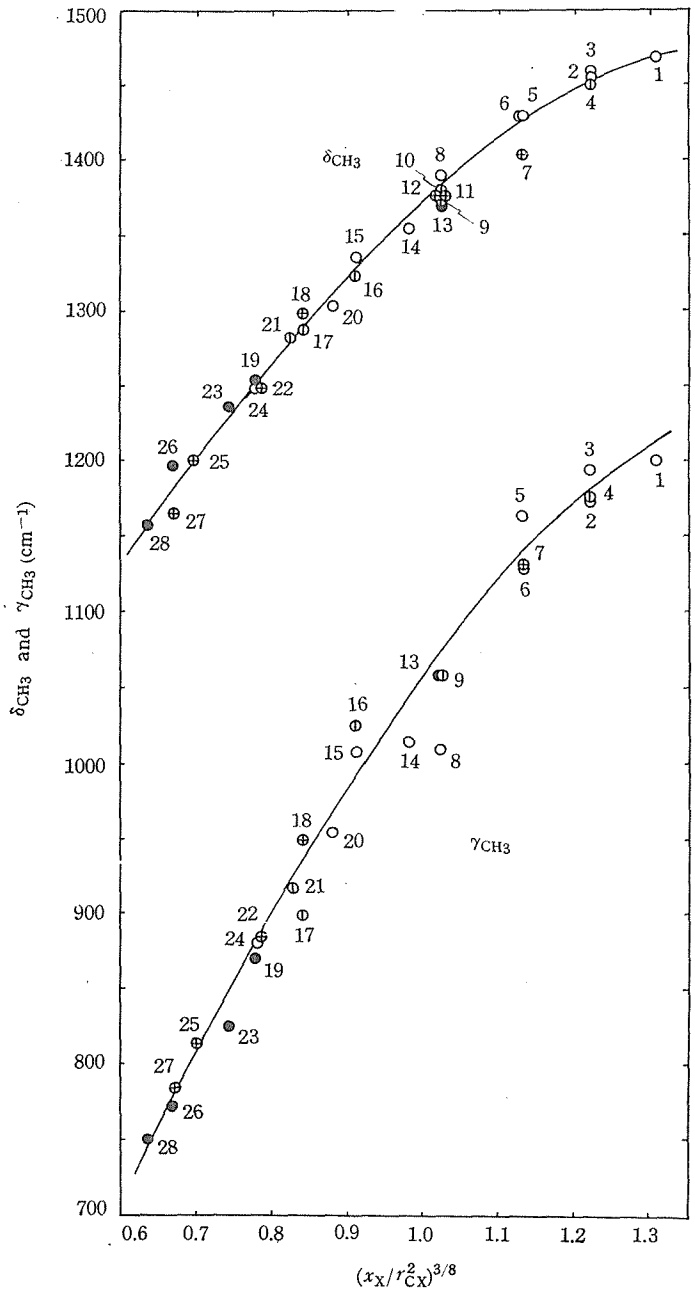

Fig. 2. Plot of δ_{CH_3} and γ_{CH_3} against $(x_X/r^2_{CX})^{3/8}$ for $(CH_3)_nXH_{m-n}$ and $(CH_3)_nXD_{m-n}$ molecules.

Numbers beside plots are those of molecules in Table 2. For symbols see Fig. 1.

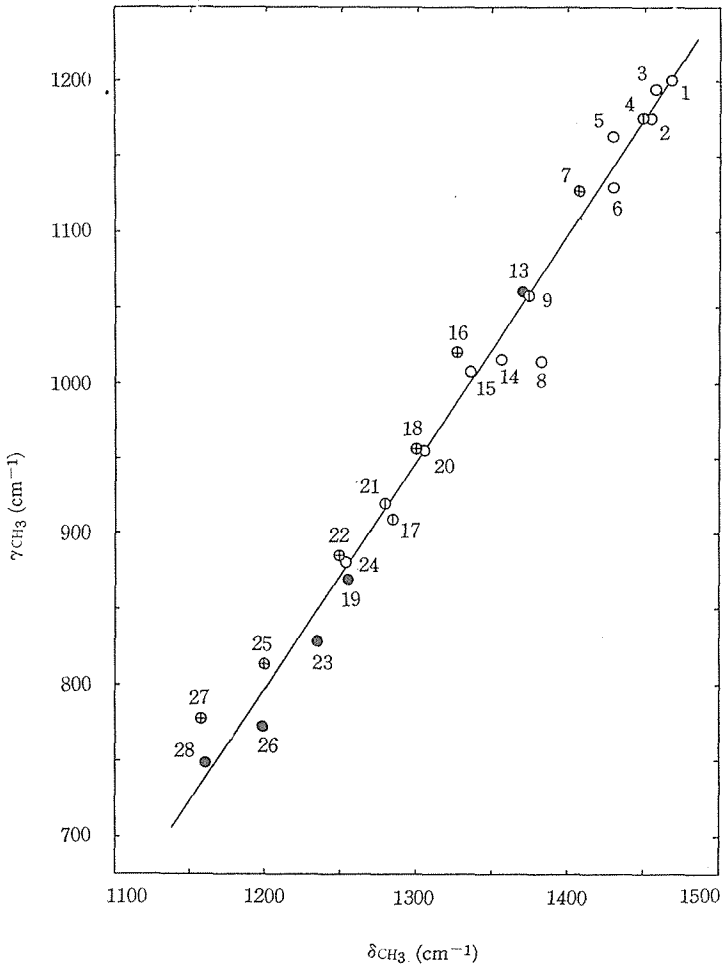

Fig. 3. Plot of γ_{CH_3} against δ_{CH_3} for $(CH_3)_n XH_{m-n}$ and $(CH_3)_n XD_{m-n}$ molecules.

Numbers beside plots are those of molecules in Table 2. For symbols s e Fig. 1.

$$4\pi^2c^2\delta_{CH_3} = G_\delta(F_{HCX}+F_{HCH}) \qquad (4)$$

and

$$4\pi^2c^2\gamma^2_{CH_3} = G_\gamma F_{HCX} \qquad (5)$$

and that F_{HCX} is expressed by a simple quadratic formula of $\log(x_X/r^2_{CX})$ (see Appendix). Here c is the velocity of light and G_δ and G_γ are diagonal elements concerning the respenctive vibrational modes in the kinetic energy matrix of the molecule. G_δ and G_γ as well as F_{HCH} are assumed to be constant throughout the methyl compounds[1] (see below).

2.2 The Symmetrical Deformation and the Rocking Frequencies of Deuterated Methyl Groups

When an atom of a molecule is replaced by an isotopic atom, it is assumed that the potential energy function and configuration of the molecule are changed by negligible amounts. Then, from the results of the preceding section, the linear dependence of δ_{CD_3} and γ_{CD_3} upon $\log(x_X/r_{CX}^2)$ may be expected to hold. Here δ_{CD_3} and γ_{CD_3} are the average frequencies of the symmetrical deformation and the rocking vibrations of the deuterated methyl group. Moreover, the correlation between the expressions for δ_{CH_3} and δ_{CD_3} and that between γ_{CH_3} and γ_{CD_3} may be given in terms of the change in respective diagonal elements of the kinetic energy matrix on deuteration of the methyl group. Then from Eqs. (4) and (5) we have

$$\delta_{CD_3}/\delta_{CH_3} = (G_\delta'/G_\delta)^{1/2} \qquad (6)$$

and

$$\gamma_{CD_3}/\gamma_{CH_3} = (G_\gamma'/G_\gamma)^{1/2}, \qquad (7)$$

where G_δ' and G_γ' are the respective diagonal elements of the kinetic energy matrix of the deuterated molecule.

Now, according to Nakagawa and Mizushima[1] G_δ and G_γ for the methyl halides can be expressed as

$$G_\delta = \underline{\frac{2\mu_H+(16/3)\mu_C}{r_{CH}^2}} \qquad (8)$$

and

$$G_\gamma = \underline{\frac{\mu_H+(1/6)\mu_C}{r_{CH}^2}+\frac{3\mu_X}{2r_{CX}^2}+\mu_C\left(\frac{3}{2r_{CH}^2}+\frac{1}{r_{CH}r_{CX}}\right)}, \qquad (9)$$

where μ_H, μ_C, and μ_X are the reciprocals of masses of the H, C, and X atoms, and r_{CH} and r_{CX} are the C–H and C–X bond lengths.* Then if we have G_δ' and G_γ' from Eqs. (8) and (9) by replacement of μ_H to μ_D with the assumption that others remain constant on deuteration of the methyl group, from Eqs. (6) and (7) the numerical values 1/1.30 and about 1/1.34** are obtained for the ratios $\delta_{CD_3}/\delta_{CH_3}$ and $\gamma_{CD_3}/\gamma_{CH_3}$ of the isotopic molecules of the methyl halides.

The plots of δ_{CD_3} and γ_{CD_3} against $\log(x_X/r_{CX}^2)$ for the $(CD_3)_nXH_{m-n}$ and $(CD_3)_nXD_{m-n}$ molecules are given in Fig. 4. The values of x_X, r_{CX}, δ_{CD_3}, and γ_{CD_3} are listed in Table 3, together with the observed frequencies of the symmetrical deformation and the rocking vibrations, from which δ_{CD_3} and γ_{CD_3} are

* The underlined parts in Eqs. (8) and (9) are independent of the X atom, and therefore G_δ is expected to be constant throughout the methyl compounds. Although G_γ consists of the underlined part and the others, μ_H of the former makes this term much larger than the latter containing the reciprocals of masses of heavier atoms. Then it seems that G_γ is nearly constant also.

** The terms concerning the X atom in Eq. (9) are not much different in numerical values among four methyl halides.

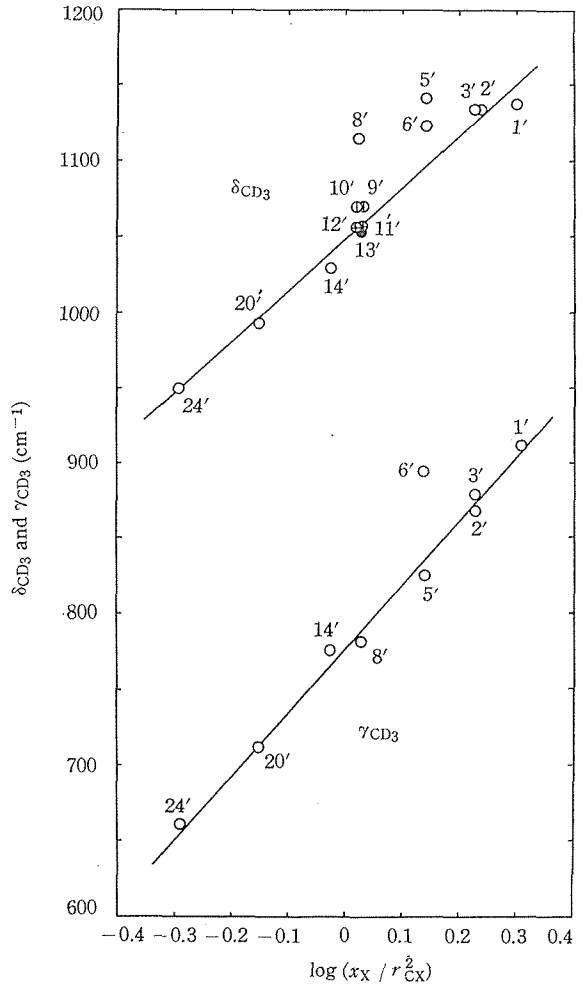

Fig. 4. Plot of δ_{CD_3} and γ_{CD_3} against $\log(x_X/r_{CX}^2)$ for $(CD_3)_nXH_{m-n}$ and $(CD_3)_nXD_{m-n}$ molecules.

Numbers beside plots are those of molecules inTable 3. For symbols see Fig. 1.

obtained by taking into consideration the degeneracy. Here r_{CX} in these molecules is assumed to be the same as that in the corresponding $(CH_3)_nXH_{m-n}$ molecules. It is seen from Fig. 4 that with some exceptions the expected linear relations of δ_{CD_3} and γ_{CD_3} against $\log(x_X/r_{CX}^2)$ are found, and can be expressed as

$$\delta_{CD_3} = 338 \log(x_X/r_{CX}^2) + 1049 \qquad (10)$$

and

$$\gamma_{CD_3} = 416 \log(x_X/r_{CX}^2) + 778\,. \qquad (11)$$

Table 3. Observed and calculated frequencies of the symmetrical deformation and the rocking vibrations of CD_3 groups in $(CD_3)_nXH_{m-n}$ and $(CD_3)_nXD_{m-n}$ molecules.

(1) No.[a]	(2) Molecule	(3) Electro-negativity[b] x_X	(4) Bond length[c] r_{CX} (Å)	Sym. CD_3 deformation frequency (cm^{-1})			(8) Deviation 100{(6)−(7)}/(6) (%)	CD_3 rocking frequency (cm^{-1})			(12) Deviation 100{(10)−(11)}/(10) (%)
				(5) Observed(Species)	(6) Average	(7) Calculated		(9) Observed(Species)	(10) Average	(11) Calculated	
1′	CD_3F	3.94	1.39	1137 (A_1)[d]	1137	1153	−1.4	911 (E)[d]	911	907	+0.4
2′	CD_3OH	3.47	1.43	1134 (A')[e]	1134	1127	+0.6	877 (A') 858 (A'')[e]	868	873	−0.6
3′	CD_3OD	3.47	1.43	1135 (A')[e]	1135	1127	+0.7	900[l] (A') 856 (A'')[e]	878	873	+0.6
5′	CD_3NH_2	3.01	1.47	1142 (A')[f]	1142[k]	1098	+3.8	740[m] (A') 910 (A'')[f]	825	838	−1.6
6′	CD_3ND_2	3.01	1.47	1123 (A')[f]	1123[k]	1098	+2.2	880 (A') 910 (A'')[f]	895[k]	838	+6.4
8′	CD_3CD_3	2.52	1.54	1158 (A_{1g}) 1077 (A_{2u})[g]	1118[k]	1058	+5.3	970 (E_g) 594 (E_u)[g]	782	789	−0.9
9′	$(CD_3)_2CH_2$	2.52	1.54	1070 (A_1, B_1)[h]	1070	1058	+1.1	——	—	789	—
10′	$(CD_3)_2CD_2$	2.52	1.54	1070 (A_1, B_1)[h]	1070	1058	+1.1	——	—	789	—
11′	$(CD_3)_3CH$	2.52	1.54	1071 (A_1) 1052 (E)[i]	1058	1058	0	——	—	789	—
12′	$(CD_3)_3CD$	2.52	1.54	1068 (A_1) 1056 (E)[i]	1060	1058	+0.2	——	—	789	—
13′	$(CD_3)_4C$	2.52	1.54	1104 (A_1) 1037 (F_2)[j]	1054	1058	−0.4	——	—	789	—
14′	CD_3Cl	3.00	1.78	1029 (A_1)[d]	1029	1041	−1.2	775 (E)[d]	775	769	+0.8
20′	CD_3Br	2.68	1.94	993 (A_1)[d]	993	999	−0.6	712 (E)[d]	712	717	−0.7
24′	CD_3I	2.36	2.14	951 (A_1)[d]	951	951	0	662 (E)[d]	662	658	+0.6

Note: a) Primes refer to the methyl-deuterium derivatives of the molecules indicated by the same numbers in Table 2.
b) Reference 8).
c) Reference 9).
d) Note d) in Table 2.
e) Reference 13).
f) Reference 11).
g) Note i) in Table 2.
h) Note k) in Table 2.
i) Note l) in Table 2.
j) E. R. Shull, T. S. Oakwood and D. H. Rank, *J. Chem. Phys.*, **21**, 2024 (1953).
k) Excluded in case of calculating the empirical formula.
l) The A' rocking and the A' OD bending modes are considerably coupled to give the 1024 cm^{-1} and 776 cm^{-1} bands. The value given here is an average of these frequencies (see text).
m) The value (913 cm^{-1}) of reference 11) is replaced by this value, according to the result[10] of the potential energy distribution in this molecule (see text).

From Eqs. (2) and (10), and Eqs. (3) and (11), the values of the ratios $\delta_{CD_3}/\delta_{CH_3}$ and $\gamma_{CD_3}/\gamma_{CH_3}$ are obtained to be 1/1.29~1/1.32 and 1/1.33~1/1.35, respectively, within the limiting values ($-0.53 \sim +0.31$) of $\log(x_X/r_{CX}^2)$ for all molecules examined in this paper. These results are in nearly good agreement with the values predicted from Eqs. (6) and (7) for the methyl halide.

In seventh and eleventh columns of Table 3, the calculated values for the symmetrical deformation and the rocking frequencies obtained from Eqs. (10) and (11) are summarized. Next respective columns are the percent deviations of the observed average frequencies from the calculated frequencies of the symmetrical deformation and the rocking vibrations.

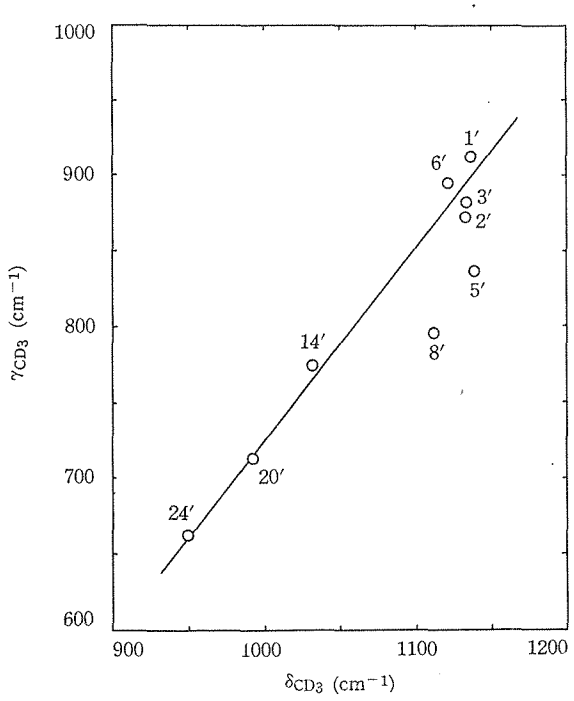

Fig. 5. Plot of γ_{CD_3} against δ_{CD_3} for CD_3XH_{m-1} and CD_3XD_{m-1} molecules.

Numbers beside plots are those of molecules in Table 3.

The relatively large deviations of the CD_3 symmetrical deformation frequency are found for CD_3NH_2, CD_3ND_2, and CD_3CD_3. In these cases, the observed frequencies are in higher frequency side than the calculated values. Since, it is reported[10] for CD_3NH_2 and CD_3ND_2 that there is considerable coupling between the CD_3 symmetrical deformatien vibration and the C–N stretching vibration at lower frequencies, the upward deviations of the CD_3 symmetrical deformation frequencies in these molecules can be interpreted on this basis. On the other hand, considering the above-mentioned results[12] that the fundamentals of CD_3CD_3

are nearly pure, it is very questionable whether the deviation of the symmetrical deformation frequency in this molecule is due to the coupling between this vibration and others. At any rate, it is interesting that the upward deviations of the symmetrical deformation frequencies are found only for the molecules in which the CD_3 symmetrical deformation frequencies are higher than the CD_3 degenerate deformation frequencies contrary to the notion that the former is is lower than the latter.

A relatively large deviation of the CH_3 rocking frequency is found for CD_3ND_2 (point group C_s). In accordance with this fact, it was pointed out[10] for this molecule that there are considerable couplings among the A' CD_3 rocking, the ND_2 wagging, and the A' CD_3 degenerate deformation vibrations, and between the A'' CD_3 rocking and the ND_2 twisting vibrations. On the other hand for CD_3NH_2, Gray and Lord[11] indentified the A' rocking vibration with a band observed at 913 cm^{-1}, but Yamaguchi[10] assigned this vibration to a band at 740 cm^{-1} according to the results of the potential energy distribution in the molecule, and therefore the latter is accepted in this paper. And, since Falk and Whalley[13] noticed that in CD_3CD the A' CD_3 rocking and the A' OD bending modes were considerably coupled to give the 1024 cm^{-1} and 776 cm^{-1} bands, we used the value $(1024+776)/2=900$ cm^{-1} as the unperturbed A' rocking frequency of this molecule.

The linear dependence of δ_{CD_3} and γ_{CD_3} upon $\log(x_X/r_{CX}^2)$ leads to a linear relation between δ_{CD_3} and γ_{CD_3} as is seen in Fig. 5 with the exception of CD_3NH_2 and CD_3CD_3.

3. GROUP ELECTRONEGATIVITY OF RADICALS

In the preceding chapter, the symmetrical deformation and the rocking frequencies of the methyl group in the $(CH_3)_nXH_{m-n}$ molecules and its deuterium derivatives were studied in relation to the type of the X atom in the groups IV—VII of the periodic table, and Eqs. (2), (3), (10), and (11) were proposed for δ_{CH_3}, γ_{CH_3}, δ_{CD_3}, and γ_{CD_3} respectively. For these molecules, in which the X atom is bonded to only the methyl group and the hydrogen atom, the frequencies calculated from the above formulas using the atomic electronegativity of X as x_X were in nearly good agreement with the observed average values. This facts may suggest that the electronegativity of the X atom is little affected bo the adjacent non-polar atoms and groups.

In the methyl compounds such as CH_3NO_2 and CH_3CCl_3, however, the electronegativity of the atom (X) directly attached to the methyl group depends on its neighbours. If the above formulas are assumed to hold for these molecules, the value of $\log(x_X/r_{CX}^2)$ and therefore the effective value of x_X may be derived from the respective average values of the symmetrical deformation and the rocking frequencies observed for these molecules. The x_X obtained in this way may be regarded as the electronegativity of the X atom perturbed by the adjacent atoms, namely the effective group electronegativity of the radical containing the X atom.

Table 4. The symmetrical deformation and the rocking frequencies of CH_3 groups in various methyl compounds and group electronegativities of radicals.

(1) No.	(2) Molecule	(3) Sym. CH_3 deform. freq. (cm^{-1}) Obs. (Species)	CH_3 rocking freq. (cm^{-1}) (4) Observed (Species)	(5) Average	(6) $\log(r_X/r_{CX}^2)$	(7) Bond length[i] r_{CX} (Å)	(8) Electro-negativity x_X
1	CH_3NO_2	1413 (A_1)[a]	1097 (B_1) 1153 (B_2)[a]	1125	0.133	1.46	2.91
2	CH_3CCl_3	1386 (A_1)[b]	1088 (E)[b]	1088	0.066	1.54	2.76
3	CH_3CHCl_2	1383 (A')[c,d]	1094 (A') 1058 (A'')[c,d]	1076	0.050	1.54	2.67
4	CH_3CH_2Cl	1385 (A')[c,d]	1050 (A') 1081 (A'')[c,d]	1066	0.042	1.54	2.62
5	CH_3CHBr_2	1384 (A')[d]	1076 (A') 1043 (A'')[d]	1060	0.035	1.54	2.58
6	CH_3CHI_2	1372 (A')[d]	1099 (A') 1040 (A'')[d]	1070	0.032	1.54	2.56
7	$CH_3C{\equiv}N$	1388 (A_1)[e]	1059 (E)[e]	1059	0.038	1.49	2.43
8	$CH_3C{\equiv}CH$	1382 (A_1)[f]	1053 (E)[f]	1053	0.036	1.46	2.32
9	CH_3SiF_3	1285 (A_1)[g]	900 (E)[g]	900	−0.236	1.88	2.06
10	$(CH_3)_2SiCl_2$	1261 (A_1, B_1)[h]	847 (A_1, A_2) 823 (B_1, B_2)[h]	835	−0.329	1.87	1.66
11	$(CH_3)_3SiCl$	1260 (A_1, E)[h]	767 (A_1, A_2) 827 ($2E$)[h]	827	−0.339	1.89	1.65

Note: a) T. P. Wilson, *J. Chem. Phys.*, **11**, 361 (1943); Symmetry C_{2v} is assumed.
b) P. Venkateswarlu, *ibid.*, **19**, 298 (1951); M. Z. El-Sabban, A. G. Meister and F. F. Cleveland, *ibid.*, **19**, 855 (1951).
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i) Reference 9).

In order to obtain this value, δ_{CH_3}, and γ_{CH_3}, which are given in Table 4 together with the observed frequencies, are plotted on Fig. 1 so that both points lie on a line parallel to the ordinate and deviate by equal amounts (if it all) in opposite directions from the two original lines (Fig. 6). In this case, the data of δ_{CH_3} and γ_{CH_3} are restricted to those for which the deviations from the original

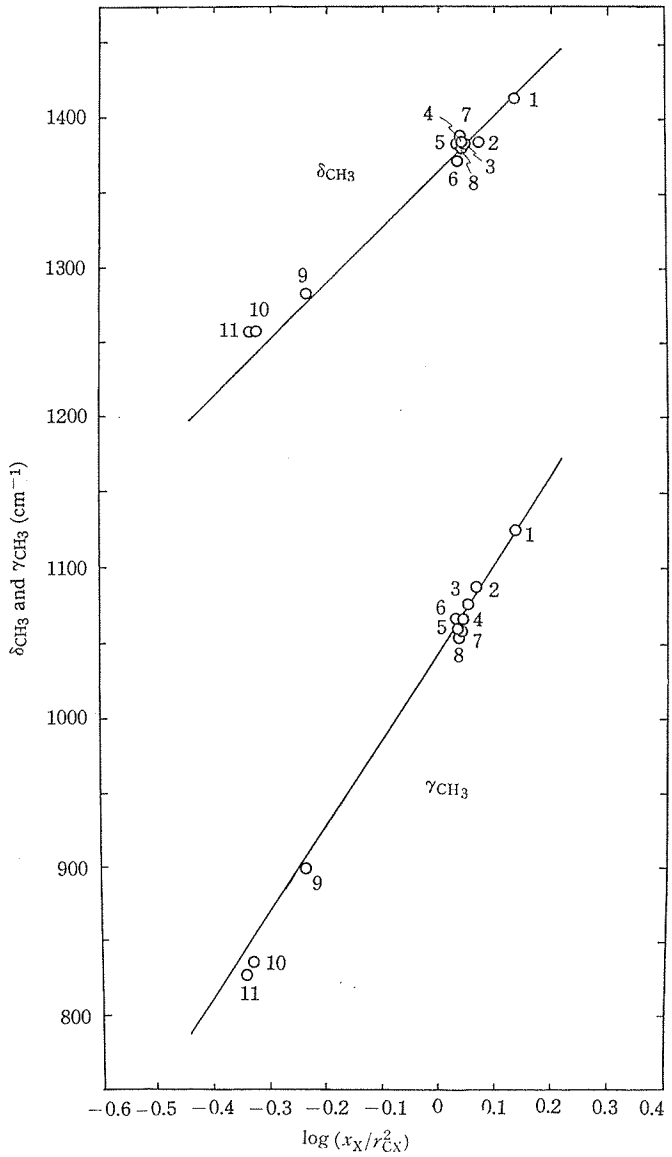

Fig. 6. Plot of δ_{CH_3} and γ_{CH_3} against $\log (x_X/r^2_{CX})$ for various methyl compounds.

Numbers beside plots are those of molecules in Table 4.

lines are relatively small (Fig. 6). Because, if the deviations are large, at least one of the symmetrical deformation and the rocking modes seem to be coupled with other modes. Thus the values of $\log(x_X/r_{CX}^2)$ are obtained as is shown in Table 4. Using this value and r_{CX}[9], the effective group electronegativity of the radical is calculated. The value of r_{CX} used and the result are also listed in Table 4.

On the other hand, numerous attempts were made to correlate spectroscopic data with electronegativities for the purpose of obtaining group electronegativities. Bell and his coworkers[14], and Kagarise[15] plotted the double bond stretching frequencies in the phosphoryl (XYZP = 0) and carbonyl (XYC = 0) derivatives against the sum of the electronegativities of the substituents and obtained sets of group electronegativities. Wilmshurst[3),16] also pointed out that the plots of $\delta_{CH_3}^2$ and $\gamma_{CH_3}^2$ of the methyl halides against the electronegativity of the halide atom yielded respective straight lines, and obtained a set of group electronegativities. Further, Dailey and Shoolery[17] showed a linear relation between the proton magnetic resonance shift in the CH_3CH_2X molecules and the electronegativity of the X atom, and obtained still another scale of group electranegativities.

In Table 5, these sets of group electronegativities are summarized in com-

Table 5. Comparison of various sets of group electronegativity.

Radical	Group electronegativity				
	Present authors[a)]	Kagarise[b)]	Dailey & Shoolery[c)]	Bell *et al.*[d)]	Wilmshurst[e)]
$-OH$	3.47	—	3.51	2.3	3.86
$-NH_2$	3.01	—	2.99	1.7	3.63
$-NO_2$	2.91	—	—	—	3.47
$-CH_3$	2.52	2.34	—	2.0	—
$-CCl_3$	2.76	2.76	—	—	3.25
$-CHCl_2$	2.67	2.62	—	—	3.22
$-CH_2Cl$	2.62	2.48	—	—	3.22
$-CHBr_2$	2.58	2.55	—	—	—
$-CHI_2$	2.56	—	—	—	—
$-C\equiv N$	2.43	—	2.52	3.3	3.11
$-C\equiv CH$	2.32	—	—	—	3.15
$-SH$	2.58	—	2.45	—	2.92
$-PH_2$	2.19	—	—	—	—
$-SiF_3$	2.06	—	—	—	2.60
$=SiCl_2$	1.66	—	—	—	—
$\equiv SiCl$	1.65	—	—	—	—
$-SeH$	2.35	—	—	—	—

Note: a) Group electronegativity of radical $-XH_{m-n}$ is assumed to be the same as atomic electronegativity of X (see text).
b) Reference 15).
c) Reference 17).
d) Reference 14).
e) Reference 16).

parison with the values obtained in this study. The values of the present authors are in comparatively good agreement with those of Kagarise[15] and of Dailey and Shoolery[17]. But Wilmshurlt's[3),16)] are considerably larger than the present author's in spite of the fact that both are obtained on the basis of the symmetrical deformation and the rocking frequencies of the methyl group.

In order to obtain the group electronegativity Wilmshurst[3)] assumed that the the linear relations of $\delta^2_{CH_2}$, and $\gamma^2_{CH_3}$ to x_X established for the methyl halides could be extended to any other methy compound. As mentioned above, however, Sheppard[4)] pointed out that the plots of δ_{CH_3} of the CH_3X groups against the atomic electronegativity of X gave a set of approximately parallel straight lines, each of which has elements in the same row of the periodic table. Moreover, it is found by the present authors that the plots of δ_{CH_3} against the logarithm of the atomic electronegativity give two sets of approximately parallel straight lines, one for each row and the othe for each column of the periodic table (Fig. 7). The values used for δ_{CH_3} and atomic electronegativity x_X are those given in Table 2. Similar relations are also found between γ_{CH_3} and $\log x_X$. These suggest that Wilmshurst's assumption is too rough. The larger values of Wilmshurst's group electronegativities could be explained by the fact that in Fig. 7 the line for the halogen substituents lies on the largest side of $\log x_X$.

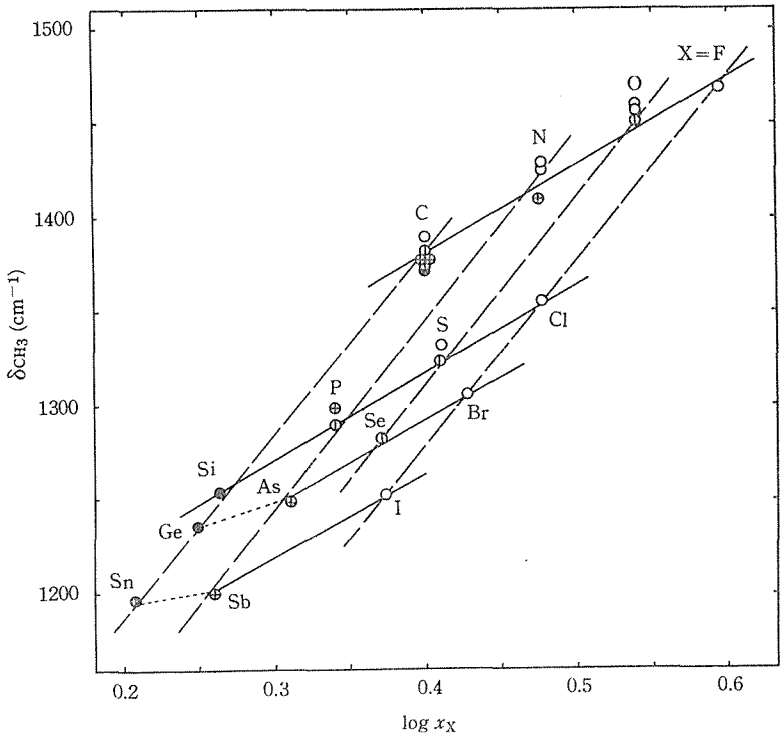

Fig. 7. Plot of δ_{CH_3} against $\log x_X$ for $(CH_3)_nXH_{m-n}$ and $(CH_3)_nXD_{m-n}$ molecules.
For symbols see Fig. 1.

The present authors wish to emphasize here that only when the symmetrical deformation and the rocking frequencies of the methyl group are plotted against $\log(x_X/r_{CX}^2)$, the respective straight lines can be obtained irrespective of the position of the X atom in the periodic table.

APPENDIX

If we put $\log(x_X/r_{CX}^2)=y$ and combine Eqs. (3) and (5), the deformation force constant of HCX angle becomes

$$F_{HCX} = \frac{4\pi^2c^2}{G_\gamma}(339y^2+1216y+1092)\times 10^3 . \qquad (1')$$

Substituting this equation into Eq. (4) and using the values $F_{HCH}=0.53$[1] and $G_\gamma=0.938$*, we have

$$\delta_{CH_3}^2 = \frac{G_\delta}{G_\gamma}(339y^2+1216y+1939)\times 10^3 . \qquad (2')$$

Considering that y is limited within the values $-0.53\sim+0.31$ for all molecules examined in this paper and that the coefficient of the quadratic term is considerably less than that of the linear term, Eq. (2′) is approximatly reduced to

$$\delta_{CH_3} = \left(\frac{G_\delta}{G_\gamma}\right)^{1/2}(437y+1392) . \qquad (3')$$

The error introduced by this approximation is less than 1.3% within the above mentioned range of y. A comparison between Eqs. (3′) and (2) gives

$$\left(\frac{G_\delta}{G_\gamma}\right)^{1/2} = 1.0\sim 0.97 . \qquad (4')$$

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* This is the average of the values calculated from Eq. (9) for all methyl halides,